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The In Situ Observation of Epitaxial Diamond Thin Film Nucleation and Growth Using Emission Electron Microscopy

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13. ABSTRACT *(Maximum 200 words)*

A miniature gas dosing apparatus for low pressure (10^{-4} Torr) diamond growth has been tested: photoelectron microscope images have been acquired under deposition conditions, and alteration in the image due to atomic hydrogen impact/reaction have been observed. Diamond growth on polycrystalline films has not been verified since incremental growth at the low rate expected will be difficult to detect on a rough substrate. Growth test on Mo(100) and (310) are underway. In situ etching of diamond in oxygen has shown that diamonds are embedded in a Mo-carbide layer which remains after etching. The pits left after etching indicate nucleation on Mo, not Mo-carbide. The observation of ordered carbon films deposition from a methane/atomic hydrogen gas stream directed at a Mo(100) single crystal surface in situ at 1000 K continues. Attempts at creating nucleation sites to specifically enhance two dimensional growth have been partially successful.

For epitaxial systems, the LEED microscope, which uses diffraction contrast to form an image, will be used to study in situ steps and ledges engineered to match the diamond lattice. Diamond (100) LEED patterns and H_2 desorption have been observed. Si(310) wafers, Mo(310) and C(310) are currently being characterized.

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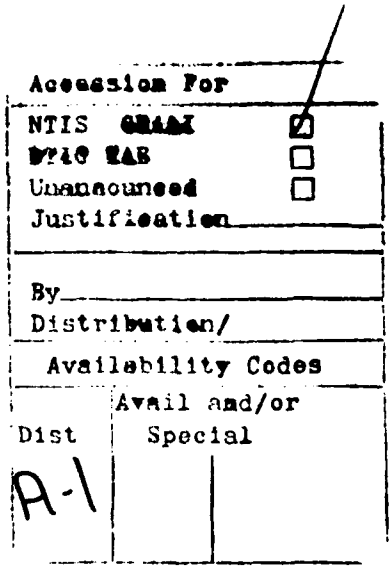

Summary of Progress:

Experimental efforts are concentrated on (1) the need to establish that conditions in our in situ growth system are sufficient for diamond growth, (2) the preparation of substrates with high step-terrace density that are suitable templates for diamond heteroepitaxy and (3) developemnt of of a two-dimensional diamond growth method.

Progress in the first of these areas has centered around a "focus-defocus" transition in our PEEM (photoelectron emission micrsocope) that may be induced by atomic hydrogen on the polycrystalline diamond surface. The effect (tentatively) confirms that carbon and atomic hydrogen are present and their influence is observable at the surface, at a temperature adequate for diamond growth. To advance effort (2), we have prepared a Mo(310) single crystal, and determined that a stable, unfaceted surface results. The Si(310) and C(310) surface have not yet been characterized, although these substrates are on hand. A systematic study of how to prepare an unreconstructed or stable faceted surface is under way. For effort (3), the study of two-dimensional carbon layer growth has been extended to include the nucletion mechanism for the effect described in the publication appended to this report.

Separate efforts directed at LEEM analysis of hydrogen induced reconstruction of the diamond C(100) surface have been conducted; no clear images of the diamond surface have been obtained in LEEM due to a severe charging/secondary electron emission from the diamond surface. LEED patterns, and the 1x1 to 2x1 transition were observed. The LEED patterns could be observed without heating; the preparation method used was suggested by Thomas et al (J. Chem. Vapor Dep. 1 (1992) 6-19): alternate boiling in chromic acid-based glass cleaner and a nitric acid bath.

An attempt at diamond growth was made on an epitaxially grown iron film on a Cu(100) crystal. Only sparse, three dimensional nucleation was observed. Several experiments on the nucleation and etching of polycrystalline diamond films have been completed in this half-year. These efforts are described in an M.S. Thesis and a Ph.D. Dissertation; the abstracts are appended.

Publications:

1. "Controlled Deposition and Lateral Growth of an Ordered Carbon Layer on Mo(100) Observed In Situ," Applied Physics Letters 61 (1992) 2984-6.

2. "A Sample Tilting Mechanism and Transfer System for High-Temperature Thin Film Deposition and UHV Electron Microscopy," Adrian Garcia and Martin E. Kordesch, J. Vac. Sci. Technol., in press (scheduled for March/April 1993 Issue).

Presentations:

1. "Electron Emission Microscopy for In Situ Studies of Diamond Surfaces and CVD Diamond Nucleation and Growth, M.E. Kordesch, Third International Symposium on Diamond Materials, Hawaii, May 1993. Submitted 1-Nov-92.

2. "Real Time In Situ Observation of Ordered Carbon Layer Growth Observed with PEEM" Adrian Garcia and Martin E. Kordesch, 39th National American Vacuum Society, Chicago, November 1992.

3. "Chemical Vapor deposition of an Ordered Carbon Monolayer on Mo(100) by the Propogation of a Two-Dimensional Wavefront" Adrian Garcia and Martin E. Kordesch, American Physical Society March Meeting, Cincinnati, March 1992.

Thesis/Dissertations:

1. Walter Whitaker III, M.S. Physics 1992 "The growth of Diamond on Epitaxial FCC Iron Overlayers: A Feasability Study".

2. Congjun Wang, Ph.D. Physics 1993 "A Photoelectron Emission Microscope Investigation of CVD Diamond Films and Diamond Nucleation"

Controlled deposition and lateral growth of an ordered monolayer of carbon on Mo(100) observed *in situ*

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A two-dimensional ordered carbon monolayer has been deposited on oxygen covered Mo(100) at 1300 K from a 5% methane in hydrogen gas mixture passed over a tungsten filament at 2300 K. The carbon layer grows laterally by occupying surface sites freed by the removal of adsorbed oxygen. A well-defined growth front is observed with photoemission electron microscopy, as well as a transitional species localized at the carbon-oxygen growth boundary.

The combination of hot filament assisted chemical vapor deposition (HFCVD) and atomic layer epitaxy methods has allowed us to observe the initial stages of epitaxial carbon deposition on a single crystal molybdenum surface *in situ* under conditions approaching those used for polycrystalline CVD diamond growth. We have already applied the photoemission microscope (PEEM) to the deposition of polycrystalline diamond films.[1]

Emission microscopy is a *high contrast* method, able to detect and image single layers of adsorbed gasses and metals on solid surfaces,[2-11] and to provide both real space images, and, in the low energy electron microscope (LEEM), a diffraction pattern[12,13] in real time at video rates.

In the photoemission microscope, variations in the photoelectron yield are the source of contrast and image intensity. For a given illumination energy (or wavelength), if the surface has a work function less than the illumination energy, there will be some ejected photoelectrons to form an image. When the work function is greater than the illumination energy, there will be no photoelectron emission, and hence no intensity in the image. In our experiment, the illumination energy is about 5.1 eV, so that the oxygen covered molybdenum surface is totally dark in the image, but the carbon covered surface is bright. By using this difference in electron yield to differentiate between oxygen and carbon covered areas of the surface, the growth of the carbon overlayer may be observed *in situ*, in real time.

The vacuum chamber and PEEM are described in Refs. 1 and 14. An accelerating field between the sample and second lens element is the basis of image formation in emission microscopy. In our microscope 10 kV are applied between the electrically grounded sample and PEEM at a 4 mm working distance. No effects due to the applied field were observed. An HFCVD arrangement is used for the deposition. The 5% methane/95% hydrogen gas mixture is introduced through a stainless steel capillary into a small ceramic tube containing the hot filament, and then through a small tube onto the substrate. The gas pressure is regulated by a variable leak valve. The total gas pressure at the specimen directly in the gas stream is estimated to be 10–100 times greater than the chamber pressure (typically 1×10^{-6} Torr).

The molybdenum crystal was cleaned by several Ar ion sputtering cycles, prolonged heating in oxygen, and annealing in ultrahigh vacuum. Low-energy electron diffraction (LEED) patterns were identical to those reported by Bauer and Poppa[15] and Gillet *et al.*[16] for oxygen covered and clean molybdenum. After the cleaning process the Mo(100) surface was covered with a single layer of oxygen, showing a $p(2\times1)$ LEED pattern, prior to exposure to the gas mixture. X-ray photoelectron spectroscopy (XPS) showed only oxygen on the Mo(100) substrate. No other contaminants were detected. In particular, no carbon signal was observed. With a degassed sample mount and an operating pressure of 1×10^{-8} Torr (mostly mass 18), an oxygen layer could be maintained for several hours at 1300 K. Carbon deposition was begun at this stage.

The images in Fig. 1 were taken from a video tape of the carbon deposition. The oxygen covered Mo(100) substrate was held at 1300 K during PEEM observation. The temperature of the substrate was measured with an infrared pyrometer.

The first micrograph shows the boundary between the carburized (light, upper left) surface and the oxygen covered (dark, lower right) surface. The second micrograph shows the formation of a bright band at the interface between the two surface regions. This band widens, and travels into the oxygen-covered area (dark).

The fact that the boundary moves forward can be observed by noting that the reaction front moves toward and surrounds the impurity nucleus (round spot with dark, raised center) in the last two micrographs. In previous experiments, it was shown that impurities such as the one shown could serve as nucleation sites for carbon deposition. These micrographs are the first observation of controlled lateral growth of a single CVD carbon monolayer.

The two wider bands to the left of the wavefront are at positions where the process was stopped and started by lowering then increasing the substrate temperature several times before these micrographs were taken. The irreversible change in the adlayer can be seen by the change in relative brightness (photoemission yield) of the bands. The width of the older bands is equal to the lateral progression of the front during the active cycle. The brightness, and hence the electronic structure,[17] of the active front is very different from the older, cooled and reheated carbon areas.

XPS analysis of the surface after a total 3.5 h deposition shows both a 100% reduction in the O 1*s* peak intensity relative to that observed initially for the oxygen cov-

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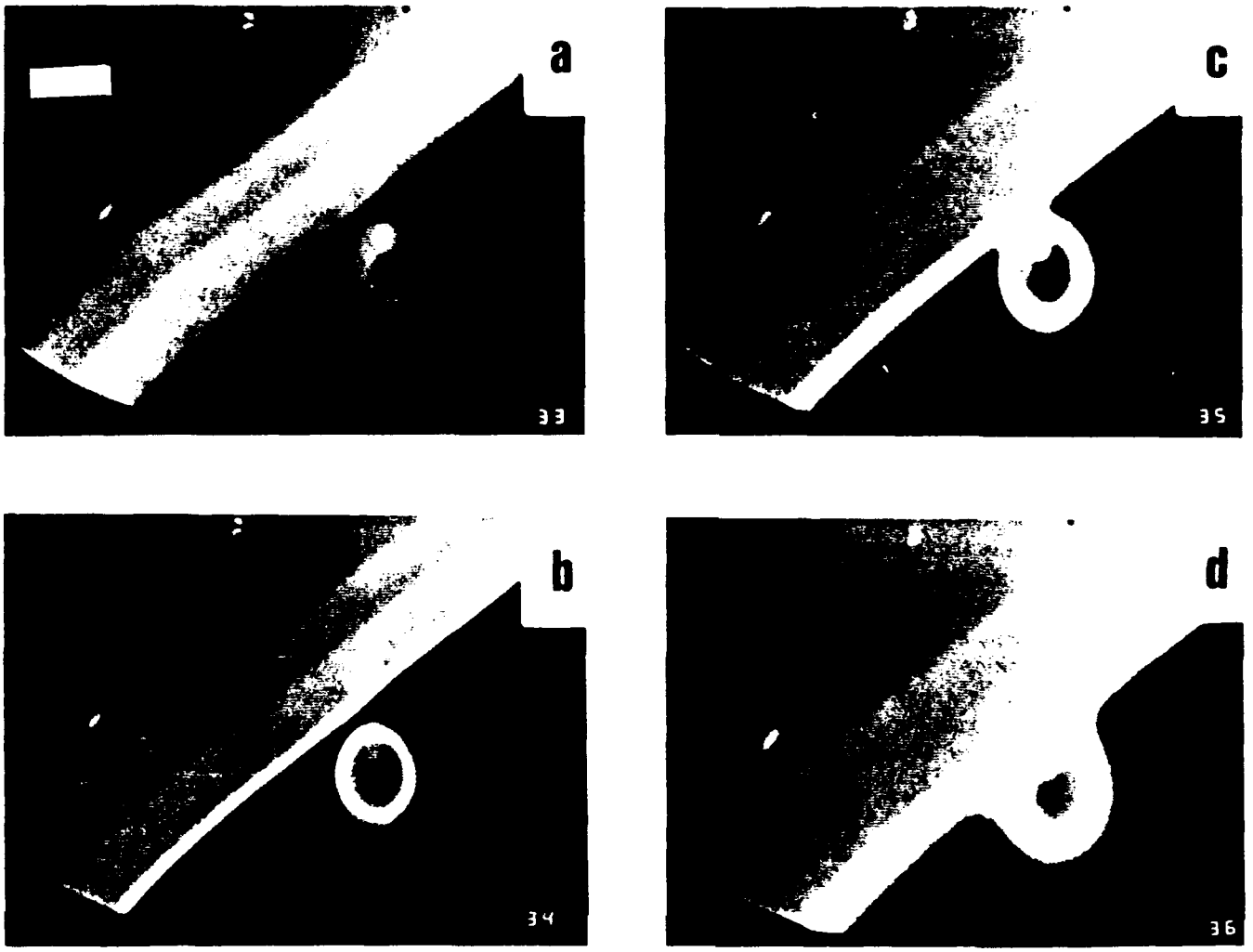

FIG. 1. PEEM micrographs of the reaction front observed during the reaction of 5% methane/95% hydrogen gas mixture with the O/Mo(100) surface. Micrograph (a) was taken with the electron beam heating turned off ($T \lesssim 700$ K). Micrographs (b), (c), and (d) were taken at $t = 0$, 30, and 50 s, respectively ($T \sim 1300$ K). The bar in (a) represents a distance of 20 μm.

ered Mo(100) surface, and the presence of carbon. The carbon overlayer showed a $p(2\times1)$ LEED pattern, with extra diffraction spots consistent with a (5×1) array of (2×1) domains.[18] The similarity of the oxygen and carbon LEED patterns suggests at least a partial site-by-site replacement of oxygen by carbon.

The micrographs in Fig. 1 show that the deposition of carbon onto oxygen covered Mo(100) can only proceed on the surface, hence an *adsorbed* carbon species must be involved. Deposition of carbon from a gas phase species, if it occurred, would be apparent as carbon islands nucleating in the oxygen covered areas of the surface. Island formation is not observed. The fact that the carbon layer grows laterally from a nucleation site at the edge of the crystal indicates that a defect or active site not present on the smooth interior parts of the crystal precipitates the reaction. Since methane does not adsorb molecularly on this surface at 1300 K, some dehydrogenation reaction is the most likely first step in the deposition process.[19]

Oxygen is strongly adsorbed on Mo(100), and desorbs near 1800 K.[15,16] At 1300 K, only a chemical reaction that weakens the Mo–oxygen bond will facilitate the displacement of oxygen. In the methane/hydrogen gas stream, such a reaction must occur during the deposition of carbon. The reaction is inhomogeneous, and proceeds across the crystal surface as a reaction front. The reaction rate increases with increasing temperature between about 700 and 1400 K. At the lower end of this temperature range, the reaction stops. The high temperature limit is the oxydation of carbon and its desorption as CO.[20]

Several pathways are available for hydrogen abstraction from methane. In the presence of a hot filament, $CH_4 + H \rightarrow CH_3 + H_2$ is a likely process, and is widely recognized as an important reaction in CVD diamond deposition.[21] In addition, the fact that oxygen is removed from the surface indicates that OH, H_2O, and O_2 must also be produced at the surface, either as a result of further hydrogen abstraction from adsorbed hydrocarbons, or that CO and other C–O compounds are formed and desorb in subsequent reaction steps.

The area of high electron yield which we have attributed to a reaction intermediate observed at the growth

interface poses several difficult questions. The width of the bright band suggests that the deposition reaction continues far beyond the carbon-oxygen boundary at the surface. The carbon ordering process in the deposited layer may be promoted by what could be a mobile species at the high yield area. Although explanations including local heating at the interface due to the exothermic recombination of hydrogen, oxygen, and water formation[22] or successive dehydrogenation of an adsorbed radical species with low work function, no conclusive spectroscopic evidence exists beyond the observation of high electron yield at the growth interface.

We have demonstrated the controlled deposition of an ordered two-dimensional carbon overlayer at the temperatures necessary for CVD diamond growth. Secondary nucleation has been successfully suppressed using a preadsorbed oxygen layer, which is removed during the reaction. The fact that oxygen is removed from the surface only at the reaction front requires the adsorption of CH as a necessary step in the deposition process. In addition, an as yet unidentified carbon species is present at the leading edge of the deposition growth front that is irreversibly altered by cooling from the deposition temperature. We believe that this process may be a first step toward heteroepitaxial growth of diamond thin films.

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A Sample Tilting Mechanism and Transfer System for High-Temperature Thin-Film Deposition and UHV Photoelectron Emission Microscopy

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Introduction

Electron microscopes are designed for complex sample manipulation relative to the electron optical axis. In a standard UHV analysis chamber, however, the sample motion requirements are usually less stringent, and some flexibility is sacrificed for sample cooling or heating, or simply for access to the sample by as many probes as possible. The newly developed Photoelectron Emission Microscope (PEEM)[1] is intended as an add-on option for a standard analysis chamber. The PEEM will fit on an 8" O.D. (203 mm) flange with a 10" (254 mm) flange face-to-sample distance, similar to LEED optics. An accurate tilting mechanism is particularly important to image quality in emission microscopes, where alignment of the sample surface normal to the microscope axis is essential for focusing (due to the shallow depth of field) and aperture contrast effects[2].

To meet the alignment requirements of our PEEM, and retain the flexibility of our analysis system (PEEM, LEED and XPS), a tilting mechanism was designed that is able to withstand prolonged heating at 1300 K. The sample is insulated from electrical ground (several kV), and either direct resistive or electron beam heating is possible. Temperature measurement by means of a thermocouple in direct contact with the sample has

been included in the design as an option.

Several sample transfer devices[3-14] have been described in recent years, albeit none of them have been intended for analysis chambers with a PEEM as the main analysis tool. Our transfer system and tilting mechanism, although primarily conceived for a chamber with vertical manipulator and 2" (50.8 mm) offset sample, may be easily adapted to meet the conditions of other surface analytical techniques and different geometrical arrangements. A particular advantage of our system is its small size; it fits through 1.5" I.D. (38mm) tubing.

Our entire apparatus (figure 1) consists of a main analysis chamber, a reaction chamber, and a magnetically driven transfer arm. The reaction chamber, in which CVD diamond films are grown, is connected to the main chamber via a 1.5" I.D. (38mm) gate valve[15]. The samples are also loaded through the reaction chamber.

In figure 2 we illustrate the sample holder attached to the precision manipulator[16] indicating its X-Y-Z translation, and rotary motions. The tilting mechanism described in the next section adds an extra motion to the sample holder about the axle. Also illustrated is the sample holder ring sitting on the fork at the end of the transfer arm.

Tilting Mechanism in the Manipulator

The overall assembly drawing of the manipulator is shown in figure 3. The ceramic bases are made from machinable ceramic[17] fired according to the manufacturer's specifications. We used a hobbyist's ceramic kiln. The rest of the manipulator is made from type 304 non-magnetic stainless steel unless otherwise specified. The tilt motion is controlled by a linear motion feedthrough[15] that drives the vertical shaft. Neither the manipulator nor the feedthrough are shown in the drawing.

The linear motion feedthrough is directly joined to the shaft. In our device the shaft was made from a 0.300" diameter (7.6 mm) rod. The stability of the vertical motion is ensured by running the shaft through the bracket holding the two ceramic bases. The slotted cross bar at the end of the shaft was made from a 0.060" thickness (1.52 mm) sheet. Two adjustment and locking nuts at the end of the shaft limit its linear motion

to prevent contact between the back end of the holder and the lower part of the bracket.

The base of the sample holder is held in place by means of a small axle with a standard 2-56 (2.2 mm) thread at one of its ends to screw in to the bracket. The axle passes through the ceramic piece as shown in figures 2 and 3. With this arrangement, the base pivots freely in the vertical plane. The base has four holes symmetrically placed around and parallel to its cylinder axis (see also figure 2). These holes are tapped from the back with a 6-32 standard thread so that the threaded metal sockets shown in the cross sectional view of figure 3 may be screwed in to the base. The sockets made with a long pin at the back end to facilitate electrical contact. These sockets can be made from thermocouple material for accurate measurement of temperature, although we have not done so. They could also be made from Ta, Mo or W for very high temperature needs. The ones we use are made from type 304 stainless steel. As shown in the left-hand side base of figure 3, there are two more holes on the base. These are intended for the support posts of the W-filament used for electron beam heating.

The link assemblies between the twin ceramic bases and the shaft's cross bar run freely and smoothly on the slots made on the cross bar (see figure 2). In this way, the precise linear motion (L.M., see figure 3) from the vertical shaft is translated into rotation of the ceramic bases about their respective axles. The result is accurate control of the sample's tilt angle with a range of 15° above and below the horizontal.

The Transfer System

The transfer arm, shown in figure 2, consists of the fork assembly attached to the end of a magnetically driven rod (0.5" diameter (12.5 mm)). The ceramic ring sits in the three-tine fork for transfer. The slots in the ceramic ring (see inset) match with the three tines of the fork. The tines are designed to push on the edge of the ceramic ring when the sample is being inserted into the base. To remove the ceramic ring, the hooks at the end of the tines lock in to the ceramic ring with a slight twist of the transfer arm. Once the fork and the ceramic ring are interlocked, it is possible to pull on the ceramic ring to remove it from the base.

The pins in the sample holder ring are made from standard 6-32 screws. As with the sockets mentioned above, a variety of materials can be used to suit particular needs. Figure 4 shows two examples of sample mounting that have been used with this system. In figure 4(a) the substrate is directly spot-welded to the screw-head-end of the pins in the sample ring. In figure 4(b), a single crystal is wired in place on a circular piece of foil spot-welded to the screw-head-end of the pins. The foil should have a hole in the center for e-beam heating.

Concluding Remarks

To facilitate the transfer, provision should be made for a window placed at an angle such that the fork and ring do not obstruct the view of the sample holder base during docking or undocking. We believe that a window placed at 45° with respect to the transfer arm at eye level will make the transfer easy enough for a single person to handle.

Since our transfer system was an addition to an already existing system, we do not have a window ideally suited to observation of the transfer. We prefer to use two people for the transfer. One person, looking at the sample through a window located at 90° with respect to the transfer arm axis, guides the docking, and another person pushes the transfer arm. The operation takes only a few minutes.

The pins in the ceramic ring do not need to fit tightly in their sockets. The attachment of the ceramic ring to the base is accomplished mainly through the small amount of friction induced by the normal misalignments of the pins in the ring and the sockets in the base.

It is a good idea to have a sample holder base identical to the one in the chamber to test the ring for major misalignment of its pins before loading the fork for transfer. A good ring will dock to the base by slightly pushing it with the transfer arm while at the same time jiggling the vertical manipulator.

Our manipulator has the capacity to hold two sample assemblies. For less roomy systems or on-axis manipulators, however, only one sample holder may be used. It is also possible to add two more sample holders to the present design by setting the second

set of holders perpendicular to the first. One of the extra holders could be used as sample storage (i.e. no wires or heater), or as a station for sample exchange. The design can also be adapted to different heating conditions and temperature ranges. A further advantage is that the sample holders are inexpensive ($\sim$ \$6 each), and are easily machined with standard tools and techniques. We have tested the reliability of our design in our experiments and found it quite satisfactory. Shop drawings may be requested from the authors.

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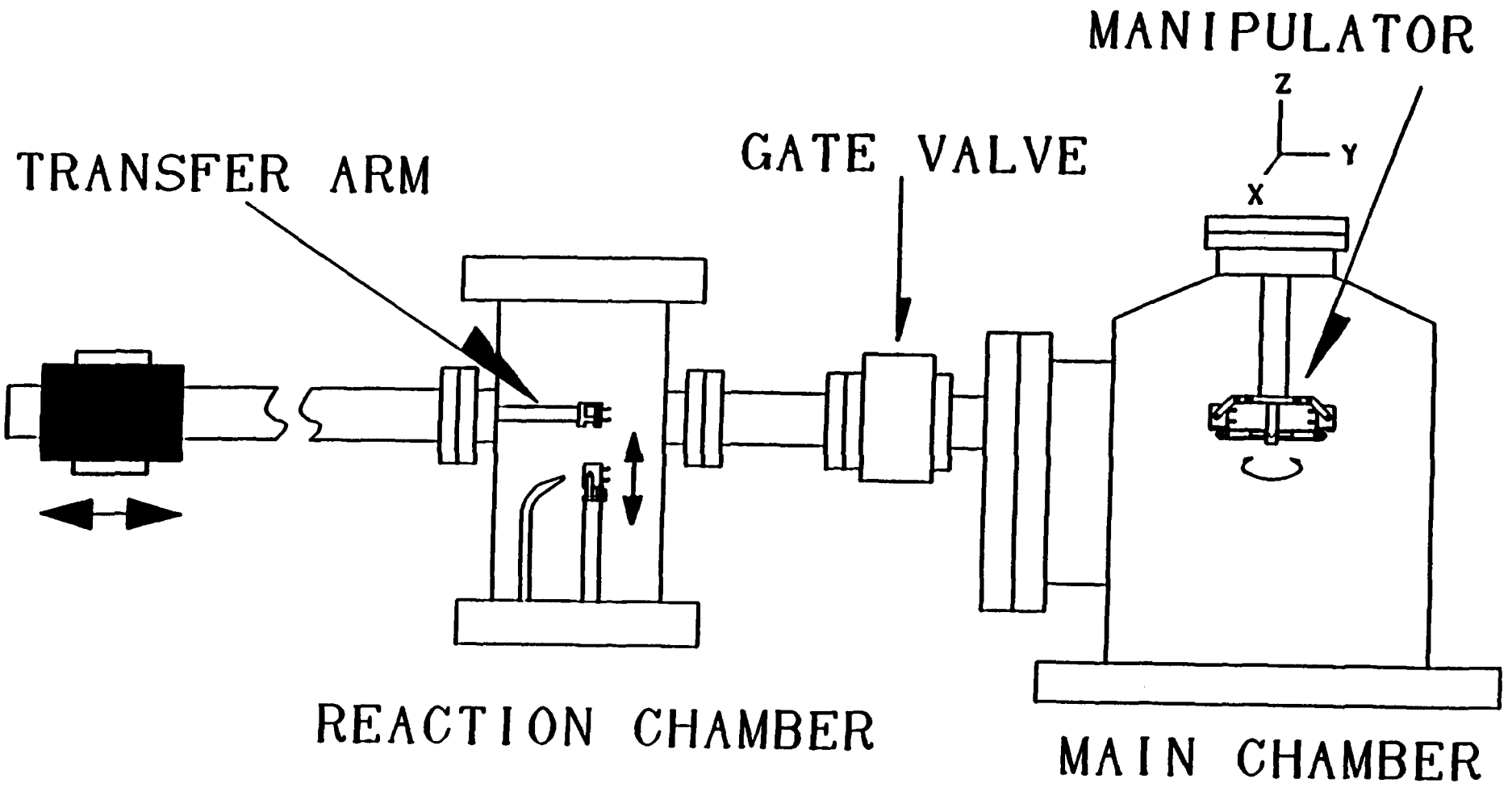
Captions

Figure 1. Schematic diagram of the experimental apparatus. Film growth is done in the reaction chamber with the substrate mounted on a ceramic ring as shown in figure 4(a). Samples may be taken from the sample holder in the reaction chamber, which is identical to those in the analysis chamber, using the three tine fork illustrated in figure 2, or they may be loaded directly to the fork trough the upper end of the reaction chamber. The sample is carried into the analysis chamber mounted in the three tine fork attached to the transfer arm. The manipulator in the main chamber has X-Y-Z translation, tilt, and rotary motion.

Figure 2. The transfer system. The fork tines fit into the slots of the ceramic ring (shown in the inset). The tines are designed to push on the ring edge when the sample is being inserted to the base. When undocking from the holder base, the tines pull on the ceramic with the small 'finger-like' hooks at their ends. The locking/unlocking of the fork on the ring is done by a slight rotation of the transfer arm.

Figure 3. Schematic representation of the tilting mechanism. The figure shows the locking nuts that limit the vertical motion of the shaft; two different cuts through the ceramic bases showing the W filament (left hand side base) and the metal sockets screwed in from the back (right hand side base); the link assembly showing the connection between the ceramic base and the cross bar (also shown in figure 2). The cross bar is screwed in place on the shaft. The bracket is attached to the manipulator by means of screws (not shown in the figure). With this assembly, the linear motion of the shaft is translated into tilting of the ceramic bases about their respective axles.

Figure 4. Examples of sample mounting using the ceramic sample holder ring. (a) A substrate is directly spot-welded to the screw-head-end of the pins at the places marked X. (b) A single crystal is wired to a circular piece of foil. The foil is spot-welded to the screw-head-end of the pins.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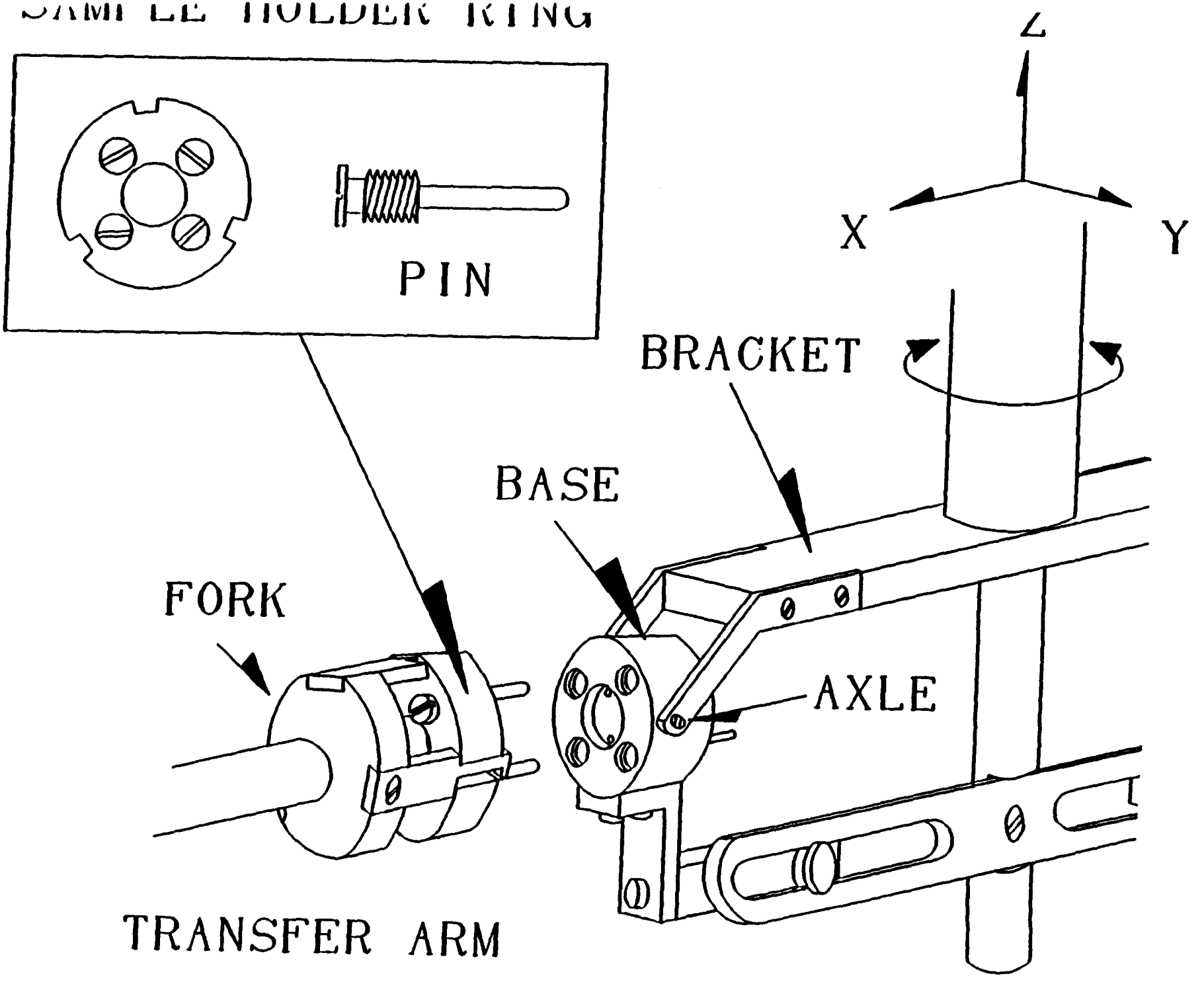
MAIN CHAMBER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BRACKET
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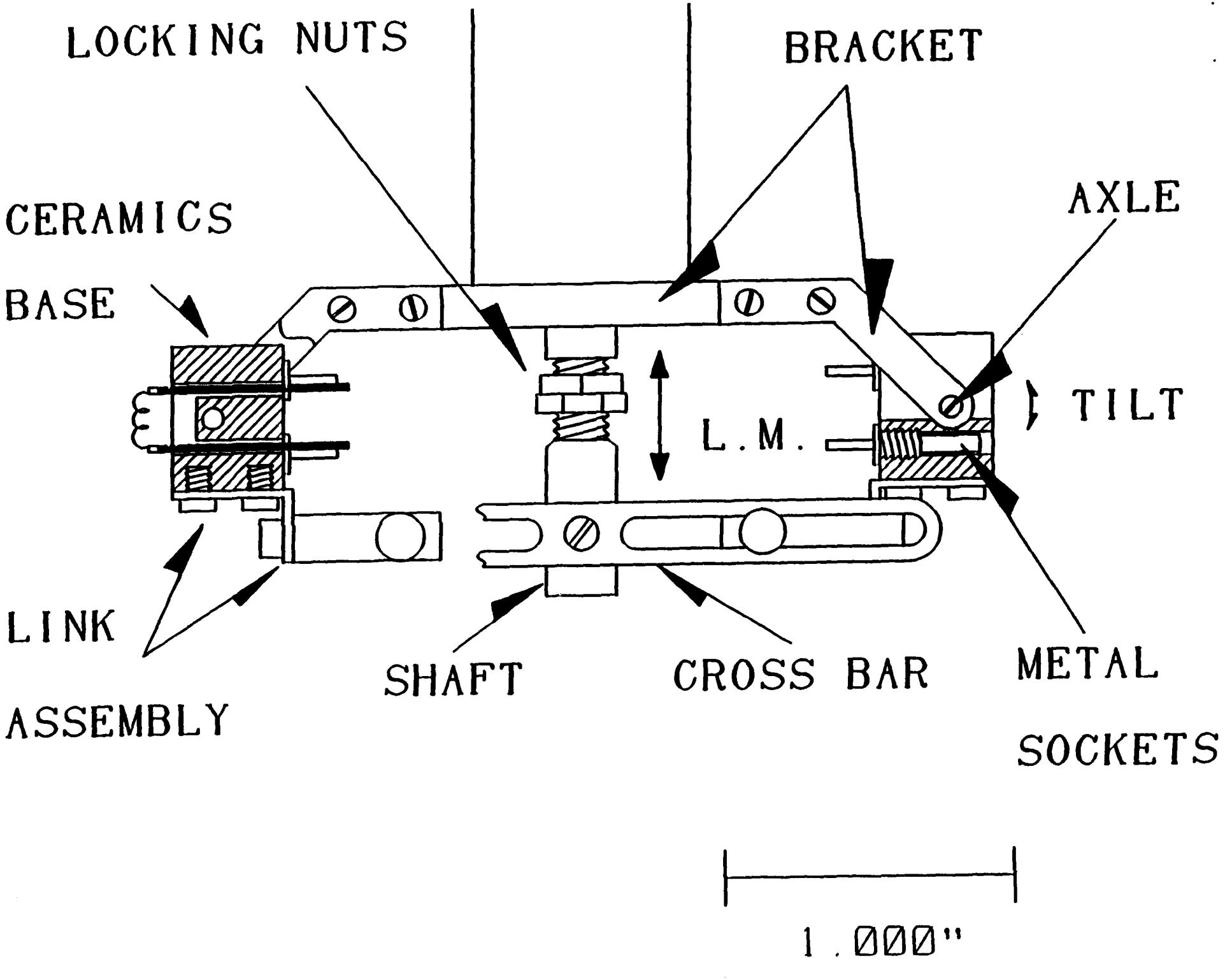
FORK
AXLE
TRANSFER ARM


LOCKING NUTS
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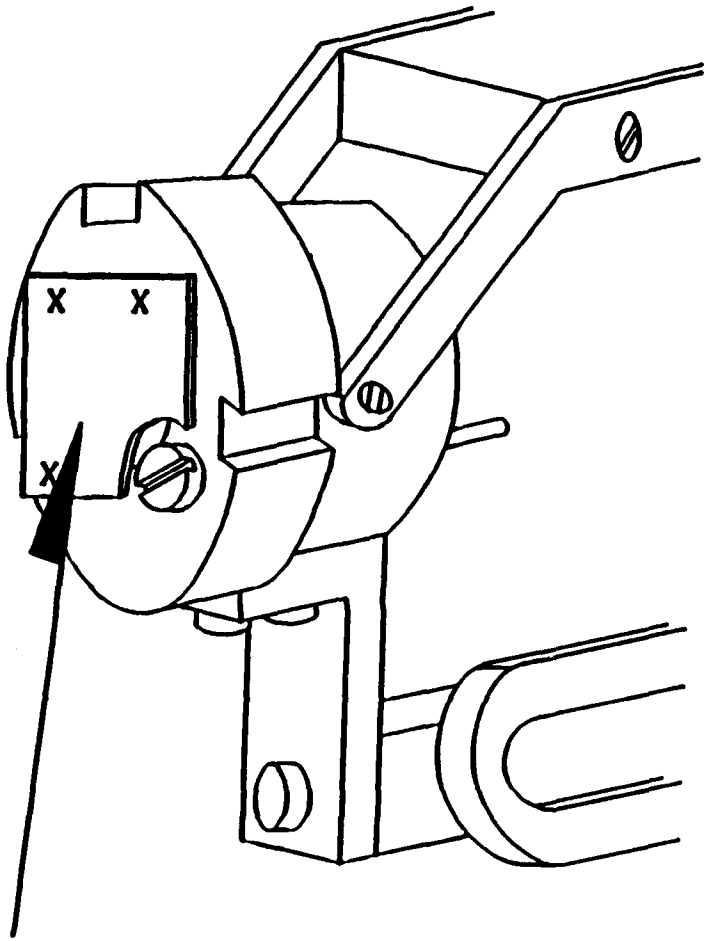
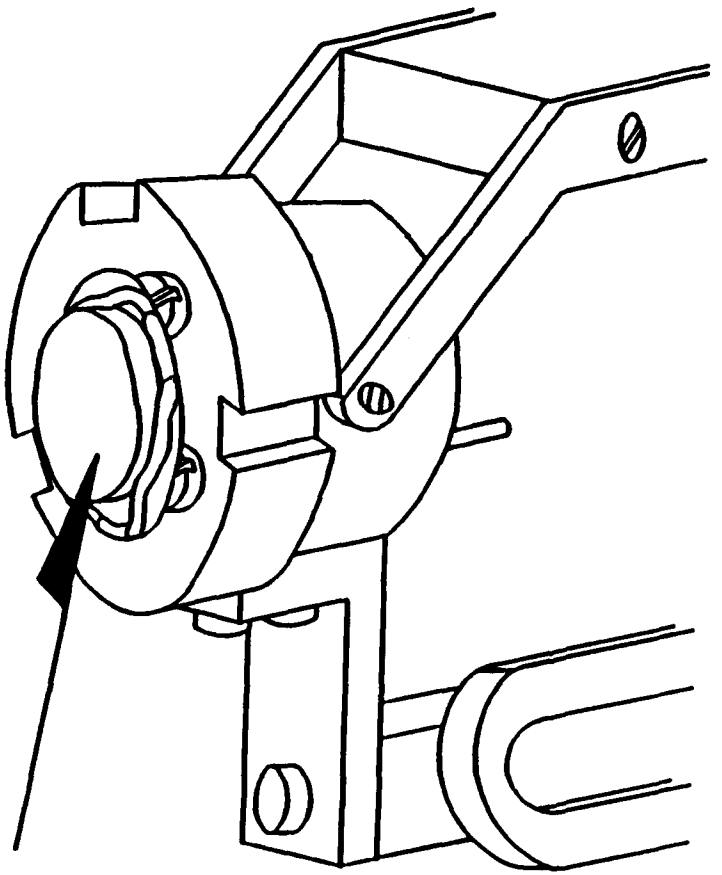
L.M.
LINK
ASSEMBLY
SHAFT
CROSS BAR
METAL
SOCKETS
1.000"



SUBSTRATE



SINGLE CRYSTAL

Electron Emission Microscopy for In Situ Studies of Diamond Surfaces and CVD Diamond Nucleation and Growth

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Introduction

The Photoelectron Emission Microscope[1,2] (PEEM) and Low Energy Electron Microscope[3] (LEEM) are direct, parallel-imaging micro- scopes that have surface-dependent image contrast mechanisms due to the shallow penetration of the illumination probes. In PEEM, the electron yield at the illumination wavelength (5.1 eV) determines image composition, in LEEM, the intensity of low energy (< 100 eV) electrons back-diffracted from the surface, as well as interference effects, are responsible for image contrast. Reflected Electron Microscopy (REM, also called Mirror Microscopy) is also possible with the LEEM apparatus. In REM, no electron penetration into the solid occurs, and an image of surface electronic potentials is obtained. The basis of emission microscopy is the "imersion lens" or "cathode lens". It should be pointed out that a field between 30-100 kV/cm is applied between the sample and the microscope in all of the emissiom microscopes discussed here[2].

These microscopes do not depend on scanning probes, and some are compatible with pressures up to 10^{-3} Torr. The unique ability to observe changes in the surface of diamond due to adsorption of gases, surface termination and structure, or conversion of diamond to graphite (as a result of work function changes or alteration in the low energy electron diffraction pattern) with these instruments in real-time, in situ, makes them attractive for diamond surface studies. The adsorption of reactants or the products of such reactions on commonly used diamond deposition substrates such as molybdenum and silicon can also be observed in situ. Lateral resolution in PEEM is about 0.1 um, limited in our case by the surface roughness of the diamond films. The "vertical resolution" can be used to image a single monolayer.

In Situ Measurements

Two types of measurement have been performed. One type involves ex situ growth in a standard HFCVD chamber and transfer to the PEEM without exposure to air, the second involves deposition during PEEM imaging. In both cases, a small hot filament doser is used to introduce gases directly onto the surface under study. A diagram is shown in figure 1.

Polycrystalline CVD diamond Films

We have used a PEEM to observe the effects of ultra violet (UV) and infra-red (IR) radiation on the CVD diamond surface, as well as etching in atomic hydrogen, oxygen and heating in ultra high vacuum. A typical polycrystalline diamond film prepared on molybdenum foil is shown in the SEM photograph in figure 2. A discontinuous film is shown in figure 3a after several minutes exposure to the combined UV and IR spectrum of our 100 W mercury arc lamp illumination source. Figure 3b shows the same film, under identical illumination conditions, exposed to a stream of atomic hydrogen produced in the miniature hot filament gas doser aimed at the sample. In figure 3b, the individual diamond crystallites are easily resolved. The resolution of the PEEM is directly proportional to the ratio of the energy spread of the emitted electrons to the acceleration voltage. When the CVD diamond surface is exposed to the UV/IR illumination, the surface is carburized, lowering the work function several eV, and decreasing the image resolution. The atomic hydrogen flux aimed at the surface etches the non-diamond carbon, and hence the diamonds in figure 3b are clearly resolved. The effect is easily reversible, and depends on the temperature of the H gas doser filament. Figure 3a and b are direct, in situ observations of non-diamond carbon etching on the CVD diamond surface. A relatively low energy probe (5 eV) is seen to severely damage the diamond surface. The UV absorption of pure diamond and common C-H compounds is negligible[4], so that it is possible that IR absorption by surface CH bonds, i.e., the loss of H surface termination, is the cause of surface decomposition to non-diamond carbon.

Heteroepitaxy

The prospects for heteroepitaxial growth of CVD diamond have also been examined in situ with PEEM. A combined CVD growth method and secondary nucleation inhibitor have been used to grow an ordered carbon monolayer on Mo(100). The oxygen covered Mo(100) surface inhibits carbon deposition from the gas phase. The oxygen layer remains intact at diamond growth temperatures. When a 5% methane in hydrogen mixture is admitted through the HF doser, a two dimensional reaction front nucleates at the edge of the crystal, and eventually passes through the PEEM field of view. A reaction front is shown in figure 4. At the leading edge, oxygen is removed by chemical reaction, and carbon is deposited in its place. An interesting feature of the deposition process is the bright band at the leading edge of the growth front. X-ray photoelectron spectra show that the oxygen signal decreases below detection levels after completion of the reaction, and is replaced by only a carbon signal. The carbon layer exhibits a (5X1) array of (2x1) domains in low energy electron diffraction. We believe such two-dimensional layer growth may be a first step towards diamond heteroepitaxy.

Several other in situ experiments have been performed using the PEEM in situ, including the investigation of nucleation density and its dependance on surface morphoiogy and carbide growth, the oxydation of diamonds, and the direct observation of diamond dissolution into the substrate at elevated temperatures in vacuum.

The low energy electron microscope is suited to investigation of single crystal samples. The Diamond(100) surface has been investigated using the electron diffraction capabilities of the LEEM. The goal of this study is the in situ observation of the reconstruction of the surface during H desorption or adsorption.

Acknowledgements

The contributions of Congjun Wang, Adrian Garcia and Joe Shovlin are gratefully acknowledged. This work was supported by the Office of Naval Research through SDIO/IST Grant No. N00014-J-1596.

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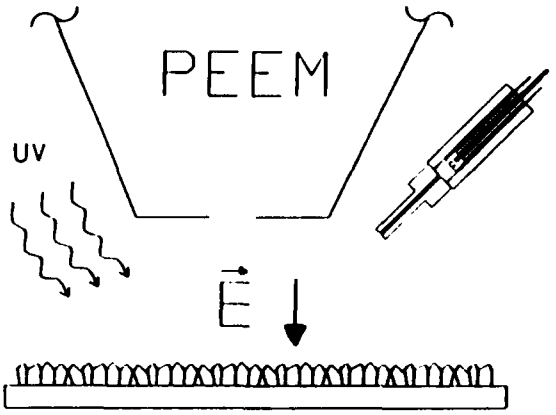

Figure 1. : PEEM, Hot Filament gas doser, and diamond film (not to scale!). The sample to PEEM distance is 4 mm. Doser to sample distance is about 20 mm. Typical field strengths are 30-50 kV/cm.

Figure 3.: a) Polycrystalline diamond film in PEEM, after several minutes exposure to UV and IR illumination. b) The same film, during hydrogen etching by gas from the hot filament doser. Film is at 300 K, hydrogen pressure is about 1x10^{-4} Torr. Field of view 250 um.

Figure 2.: Scanning electron micrograph of a typical diamond film grown in our HFCVD chamber. Bar is 1 um.

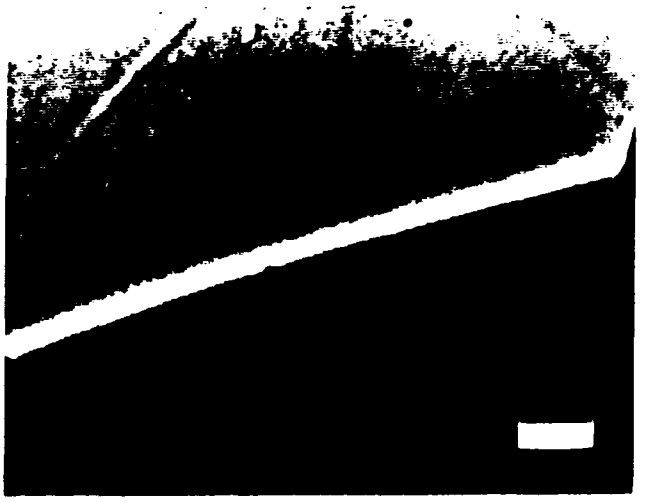

Figure 4.: Reaction front observed in situ with PEEM on Mo(100). The (light) upper half of the photograph is the ordered carbon film, the lower (dark) half is oxygen covered. The contrast is due to the fact that the oxygen covered Mo surface has a work function greater than the illumination wavelength. The bright band at the center moves to the toward the lower right during the reaction. Sample temperature is 1300 K, gas pressure 1x10^{-6} Torr 5% methane in hydrogen, passed through the hot filament doser. Bar is 20 um.

A1

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Abstract Submitted
for the 1992 March Meeting
16-20 March 1992

Suggested Session Title:
Surfaces: Metallic

March Sorting Category:
30e

Chemical Vapor Deposition of an Ordered Carbon Monolayer on Mo(100) by the Propogation of a Two-Dimensional Reaction Wavefront. Adrian GARCIA and Martin E. KORDESCH, Ohio U. -- The reactive deposition of carbon on an oxygen-covered Mo(100) single crystal surface has been observed in situ with photoelectron emission microscopy (PEEM). The Mo(100) surface is heated to 1000 K and covered with a single monolayer of atomic oxygen. LEED and XPS data confirm the O-layer purity and coverage. A stream of 5% methane in hydrogen is directed at the surface over a hot W filament which dissociates the hydrogen. The effective pressure is about 10^{-4} Torr. The deposition of carbon on the Mo surface can be observed as a travelling, wave-like reaction front, where oxygen is consumed at the leading edge, and carbon is deposited at the trailing edge. The deposited carbon layer gives a C(2x2) LEED pattern. The wave front extends over several mm, without secondary nucleation of carbon on the oxygen covered surface. Implications for atomic layer epitaxy of diamond and the dynamics of the observed reaction will be discussed.

Submitted by

Martin E. Kordesch
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Ohio University
Athens, Ohio 45701

Prefer Standard Session

Abstract Form

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Start First Line Here — Underline or bold Title and Speaker's Name

JS1

Real-time In Situ Observation of Ordered Carbon Layer Growth Observed with Photoemission Electron Microscopy, **Adrian Garcia** and Martin E. Kordesch, Ohio University, Athens, OH 45701

The reactive deposition of carbon from 5% methane/95% hydrogen gas mixture on oxygen covered Mo(100) has been observed *in situ* at 1300 K using photoemission electron microscopy. The gas mixture was first passed over a hot W filament; these conditions approximate those typically used for diamond CVD. Local pressure at the substrate is about 10^{-4} torr. The Mo(100)-p(2 × 1)-O surface is stable at this temperature, and blocks carbon deposition. Defects at the crystal edges, however, nucleate a chemical reaction that involves a site-for-site replacement of oxygen by carbon. The reaction front extends over several mm, with a transient species at the leading edge. Images of the fronts, LEED and XPS data for the deposited layer will be presented, as well as possible reaction mechanisms.

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The Growth of Diamond on Epitaxial FCC Iron Overlayers: A Feasibility Study

by
Walter E. Whitaker, III

Abstract

A film of iron was grown epitaxially on Cu(100) at room temperature. The structure was checked with LEED. Using Hot Filament CVD, non-epitaxial diamond was grown on the film, yielding a nucleation density of 3.7×10^6 /cm^2 This was verified by ESCA. PEEM and SEM were also used to examine the surface.

Submitted in Partial Fulfillment of The Requirements for
The Degree of Master of Science

Project Advisor: Martin Kordesch

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9 June 1992

WANG, CONGJUN. Ph.D. March 1993. Physics

A Photoemission Electron Microscope Investigation of CVD Diamond films and Diamond Nucleation.

Director of Dissertation: Dr. Martin E. Kordesch

CVD diamond nucleation is investigated using the hot filament technique. The stability of CVD diamond at elevated temperatures in vacuum, O_2, and atomic hydrogen environments are studied using photoemission electron microscopy (PEEM) combined with in-vacuo x-ray photoelectron spectroscopy (XPS). Dissolution, oxidation, and atomic hydrogen etching processes of CVD diamond are observed in real-time. Low field cold electron emission from CVD diamond films has been observed for the first time in PEEM.

Nucleation density on polished Mo substrates could be increased form 10^4 to $10^8/cm^2$. Heating the substrate to 870°C in vacuum prior to deposition, or above 1000°C at the beginning of deposition, reduced nucleation by more than 100-fold. Reduction in nucleation sites is attributed to annealing. Nucleation on Mo_2C substrates was found to be very poor ($10^4/cm^2$), which shows carbide alone does not promote nucleation. Carbide formation may remove nucleation sites.

CVD diamond was found to dissolve into the Mo substrate in vacuum at about 1200°C. XPS showed formation of Mo_2C when the diamond dissolved. Diamond

oxidation to gas phase products occurred directly at about 600°C, with no observable participation by the substrate. No detectable etching by atomic hydrogen at a pressure of 1 x 10^{-4} torr was observed.

Boron doped and "pure" CVD diamond films were found to emit electrons at room temperature under the action of the accelerating electric field of the PEEM (about 30 Kv/cm) without photon excitation. The mechanism underlying this phenomenon was investigated with PEEM and by studying the emission current-vs-voltage characteristics of the CVD diamond films. Morphology and crystalline orientation were found to play only a minor role. Impurities in the CVD diamond structure lowers the potential barrier substantially; tunneling of electrons into the vacuum is facile. The effective work function of the emitting CVD diamond films is measured to be between 0.1 and 0.2 eV.

Approved Martin E. Mendez

Assistant Professor of Physics